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(54) METHOD FOR DESULFURIZING HYDROCARBON OIL AND METHOD FOR PRODUCING HYDROGEN FOR FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for desulfurizing efficiently an organic sulfur compound-containing hydrocarbon oil by adequately accelerating the oxidative reaction of the sulfur compound; and a method for producing hydrogen for a fuel cell.

SOLUTION: The method for desulfurizing an organic sulfur compound-containing hydrocarbon oil comprises (A) a step of oxidating the hydrocarbon oil with an oxidative agent using a microchannel reactor and (B) a step of eliminating an organic sulfur oxide compound yielded in the process (A). The method for producing hydrogen for a fuel cell comprises contacting the above desulfurized hydrocarbon oil with a partial oxidation catalyst, an autothermal reforming catalyst or a steam reforming catalyst.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The desulfurization approach of the hydrocarbon oil characterized by giving the process which oxidizes an organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor, and the process which removes the organic sulfur oxidation compound obtained at the (B) above-mentioned (A) process.

[Claim 2] (A) The desulfurization approach of a hydrocarbon oil according to claim 1 that the micro channel reactor in a process is a with an equivalent diameter [of 1mm or less] thing.

[Claim 3] The desulfurization approach according to claim 1 or 2 which an organosulfur compound is contacted to an adsorbent and carries out adsorption treatment.

[Claim 4] (A) The desulfurization approach of a hydrocarbon oil according to claim 1 to 3 of giving the process which contact processing liquid with the adsorbent obtained at the (C) above-mentioned (B) process is further contacted to a devulcanizing agent, and removes a residual sulfur compound after giving a process and the (B) process.

[Claim 5] The desulfurization approach of a hydrocarbon oil according to claim 1 to 4 that an organosulfur compound content hydrocarbon oil is LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, a waste plastic oil, or biotechnology fuel.

[Claim 6] The oxidizer in a process (A) Oxygen, air, a nitrogen tetroxide, ozone, chlorine, A bromine, sodium metaperiodate, a potassium dichromate, potassium permanganate, A chromic anhydride, a hypochlorous acid, a hydrogen peroxide, a peracetic acid, a hydrogen-peroxide + acetic acid, A performic acid, a hydrogen-peroxide + formic acid, a meta-chloro perbenzoic acid, a hydrogen-peroxide + meta-chloro benzoic acid, A fault chloroacetic acid, a hydrogen-peroxide-solution + chloroacetic acid, fault dichloroacetic acid, hydrogen-peroxide + dichloroacetic acid, A fault trichloroacetic acid, a hydrogen-peroxide + trichloroacetic acid, fault trifluoroacetic acid, The desulfurization approach of the hydrocarbon oil according to claim 1 to 5 which is chosen from hydrogen-peroxide + trifluoroacetic acid, fault meta-sulfonic acid, hydrogen-peroxide + meta-sulfonic acid, a fault salicylic acid, a hydrogen-peroxide + salicylic acid, persulfuric acid, and a hydrogen-peroxide + sulfuric acid and which is a kind at least.

[Claim 7] (B) The desulfurization approach of the hydrocarbon oil according to claim 1 to 6 which is a kind at least that the adsorbent in a process is chosen from a porosity inorganic oxide, activated carbon, and porosity insolubility synthetic resin.

[Claim 8] (C) The desulfurization approach of the hydrocarbon oil according to claim 4 to 7 which is the thing with which the devulcanizing agent in a process comes at least to support a kind of metallic element chosen from nickel, Ag, Cr, Mn, Fe, Co, Cu, Zn, Pd, Ir, Pt, Ru, Rh, and Au to porosity support.

[Claim 9] (B) The desulfurization approach of a hydrocarbon oil according to claim 1 to 8 of making an adsorbent contacting at the temperature of the range of -40-100 degrees C in a process.

[Claim 10] (C) The desulfurization approach of a hydrocarbon oil according to claim 4 to 9 of making a devulcanizing agent contacting at the temperature of the range of -40-220 degrees C in a process.

[Claim 11] The manufacturing approach of the hydrogen for fuel cells characterized by making a partial oxidation catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst in contact after desulfurizing an organosulfur compound content hydrocarbon oil by the approach according to claim 1 to 10.

[Claim 12] The manufacture approach of the hydrogen for fuel cells according to claim 11 that a partial oxidation catalyst, an autothermal reforming catalyst, and a steam-reforming catalyst are a nickel system or a ruthenium system catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the desulfurization approach of a hydrocarbon oil, and the manufacture approach of the hydrogen for fuel cells. This invention relates to the approach of manufacturing the hydrogen for fuel cells efficiently, in more detail using the approach of fully advancing oxidation reaction of this sulfur compound, and desulfurizing it efficiently, and the hydrocarbon oil by which desulfurization processing was carried out by this approach by oxidizing an organosulfur compound content hydrocarbon oil using a micro channel reactor.

[0002]

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbon oils, such as naphtha of a petroleum system and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan.

[0003] When using a fuel cell for a noncommercial use or automobiles, the above-mentioned hydrocarbon oil is liquefied at ordinary temperature ordinary pressure, and since the distribution system is fixed, it is advantageous [the thing of a petroleum system / a gas station, a dealer, etc.] as sources of hydrogen the top where storage and handling are easy. However, such a hydrocarbon oil has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this hydrocarbon oil, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon oil. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon oil, it needs performing desulfurization processing to this hydrocarbon oil, and making long duration reduce a sulfur content content below in the rear-spring-supporter 1 weight ppm from the point of a catalyst life.

[0004] Conventionally, the sulfur compound contained in it is oxidized with an oxidizer as the desulfurization approach of a petroleum fraction, and in order to promote the reaction of the approach (JP,4-72387,A) of removing using lifting of the melting point or the boiling point or a sulfur compound, and an oxidizer, the method (JP,11-140462,A) of using an oxidation catalyst etc. is learned. However, when applying these approaches to desulfurization of an organosulfur compound content hydrocarbon oil, it is the actual condition that sufficient oxidization

effectiveness is not achieved since the sulfur concentration in this hydrocarbon oil is low, and a sulfur content cannot be reduced to practical level. Moreover, in oxidation reaction of a sulfur compound, although to perform mixing with a petroleum fraction and an oxidizing agent and churning using a homogenizer etc. was tried (JP,11-140462,A), since the reaction rate was slow, there was a problem that oxidation reaction could not fully be advanced, in this case.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of manufacturing the hydrogen for fuel cells efficiently, using the approach of fully advancing oxidation reaction of this sulfur compound, and desulfurizing an organosulfur compound content hydrocarbon oil efficiently under such a situation, and the hydrocarbon oil by which desulfurization processing was carried out by this approach.

[0006]

[Means for Solving the Problem] The result of having repeated research wholeheartedly in order that this invention persons might attain the aforementioned object, By removing an organosulfur compound by technique, such as adsorption, an extract, and distillation, and making a devulcanizing agent contact if needed further, after oxidizing an organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor It found out that the hydrogen for fuel cells could be manufactured efficiently that desulfurization processing can be carried out efficiently and by carrying out refining processing of the hydrocarbon oil by which desulfurization processing was carried out by this approach. This invention is completed based on this knowledge.

[0007] Namely, the process at which this invention oxidizes (A) organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor, The organic sulfur oxidation compound obtained at the (B) above-mentioned (A) process And adsorption, an extract, The desulfurization approach of the hydrocarbon oil characterized by giving the process which contact processing liquid with the adsorbent further obtained at the (C) above-mentioned (B) process is contacted to a devulcanizing agent the process which is made to remove by technique, such as distillation, and removes a sulfur compound, and if needed, and removes a residual sulfur compound is offered. Moreover, this invention also offers the manufacture approach of the hydrogen for fuel cells characterized by making a partial oxidation catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst contact, after desulfurizing an organosulfur compound content hydrocarbon oil by said approach.

[0008]

[Embodiment of the Invention] The process which oxidizes (A) organosulfur compound content hydrocarbon oil with an oxidizer in the desulfurization approach of the hydrocarbon oil of this invention, (B) The organosulfur compound in the oxidation-treatment liquid obtained at the above-mentioned (A) process The process which contacts contact processing liquid with the adsorbent further obtained at the (C) above-mentioned (B) process to a devulcanizing agent is given the process which makes (namely, an organic sulfur oxidation compound) remove by technique, such as adsorption, an extract, and distillation, and if needed. As an organosulfur compound content hydrocarbon oil with which the approach of this invention is applied, LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL (Gas to Liquid), a waste plastic oil, biotechnology fuel, etc. can be mentioned, for example.

[0009] In these, kerosene is suitable as a raw material for the hydrogen manufacture for fuel cells. Next, each process is explained.

(A) This process is a process which oxidizes the aforementioned organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor as **. Although the micro channel reactor used in the process concerned is a reactor with the passage of an equivalent diameter smaller than 500 micrometers as indicated by "Erdoel Erdgas Kohle", the 114th volume, and the 578th page (1998), in this invention, 1mm or less of the equivalent diameter of the passage of this reactor is sufficient. Moreover, the micro channel reactor which gave the mixed function can also be used.

[0010] Moreover, as an oxidizing agent, the thiophenes contained in the hydrocarbon oil that

what is necessary is just what can oxidize to a sulfoxide or a sulfone. It is not restricted especially. For example, oxygen, air, a nitrogen tetroxide, ozone, chlorine, a bromine, Sodium metaperiodate, a potassium dichromate, potassium permanganate, A chromic anhydride, a hypochlorous acid, a hydrogen peroxide, a peracetic acid, a hydrogen-peroxide + acetic acid, A performic acid, a hydrogen-peroxide + formic acid, a meta-chloro perbenzoic acid, a hydrogen-peroxide + meta-chloro benzoic acid, A fault chloroacetic acid, a hydrogen-peroxide-solution + chloroacetic acid, fault dichloroacetic acid, hydrogen-peroxide + dichloroacetic acid, A fault trichloroacetic acid, a hydrogen-peroxide + trichloroacetic acid, fault trifluoroacetic acid, hydrogen-peroxide + trifluoroacetic acid, fault meta-sulfonic acid, hydrogen-peroxide + meta-sulfonic acid, a fault salicylic acid, a hydrogen-peroxide + salicylic acid, persulfuric acid, a hydrogen-peroxide + sulfuric acid, etc. can be used. One sort of these oxidizers may be used and they may be used combining two or more sorts. Moreover, the amount of the oxidizer used should just be at least 1Eq to 1Eq of organosulfur compounds in a hydrocarbon oil. Although a room temperature is enough as oxidation-treatment temperature, it may warm suitably as occasion demands and you may oxidize.

[0011] (B) Contact the oxidation-treatment liquid obtained at the process aforementioned (A) process to an adsorbent, and explain the process which carries out adsorption treatment of the sulfur compound. As an adsorbent used in the process concerned, a porosity inorganic oxide, activated carbon, porosity insolubility synthetic resin, etc. are mentioned. These adsorbents may come to support a suitable metallic element. As the above-mentioned porosity inorganic oxide, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, clay, clay, diatomaceous earth, etc. are mentioned preferably, for example. Although there is especially no limit as a configuration of this adsorbent, the configuration of powder, a pellet, a tablet, a bead, etc. is desirable.

[0012] In this invention, one sort of said adsorbent may be used and it may be used combining two or more sorts. As temperature at the time of contacting a hydrocarbon oil to this adsorbent, the range of -40-100 degrees C is desirable. If there is a possibility that the fluidity of a hydrocarbon oil may fall at less than -40 degrees C, and this temperature may become inadequate [the adsorption treatment of a sulfur compound] and it exceeds 100 degrees C, there is an inclination for the adsorption capacity of an adsorbent to fall and it is not desirable.

[0013] (C) It is the process which ** is the process to which this process is given if needed, contacts contact processing liquid with the adsorbent obtained at the aforementioned (B) process to a devulcanizing agent, and removes a residual sulfur compound. By giving this process, the sulfur content content in a hydrocarbon oil can be reduced further. There is especially no limit as a devulcanizing agent used for the process concerned, and an adsorption devulcanizing agent other than an adsorbent, a hydrodesulfurization catalyst, etc. in the aforementioned (B) process can be used. The catalyst which comes at least to support a kind of metallic element: chosen, for example from nickel, Ag, Cr, Mn, Fe, Co, Cu, Zn, Pd, Ir, Pt, Ru, Rh, and Au to porosity support here as an adsorption devulcanizing agent other than the adsorbent in the aforementioned (B) process is desirable. The catalyst which comes to support especially nickel and/or Ag is suitable. These adsorption devulcanizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction processing beforehand. Moreover, when using a hydrodesulfurization catalyst as this devulcanizing agent, little addition of the hydrogen can be carried out.

[0014] In this invention, one sort of said devulcanizing agent may be used and it may be used combining two or more sorts. As temperature at the time of contacting a hydrocarbon oil to this devulcanizing agent, the range of -40-220 degrees C is desirable. If there is a possibility that the fluidity of a hydrocarbon oil may fall at less than -40 degrees C, and it may become inadequate desulfurization removing [of a sulfur compound] this temperature and it exceeds 220 degrees C, there is an inclination for the adsorption capacity of a devulcanizing agent to fall, and it is not desirable. Thus, the sulfur content in an organosulfur compound content hydrocarbon oil can be more preferably reduced below in the 0.2 weight ppm below the 0.5 weight ppm below the 1 weight ppm.

[0015] In the manufacture approach of the hydrogen for fuel cells of this invention, after

desulfurizing an organo- or compound content hydrocarbon oil by the above-mentioned approach, the hydrogen for fuel cells is manufactured by making an autothermal reforming catalyst, a partial oxidation catalyst, or a steam-reforming catalyst contact. As these autothermal reforming catalysts, a partial oxidation catalyst, or a steam-reforming catalyst, a nickel system or a ruthenium system catalyst is suitable. Moreover, although a well-known approach can be conventionally used as a partial oxidation method, autothermal reforming, and a steam reforming process, a steam reforming process is advantageous in these.

[0016] Next, the manufacture approach of the hydrogen by the steam reforming process is explained. As a steam-reforming catalyst used in this steam reforming process, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. The above-mentioned support metal may make a kind support, and may be made to support combining two or more sorts. In these catalysts, the thing (ruthenium system catalyst) which made especially the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large. In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 – 20% of the weight of the desirable range on support criteria. If there is a possibility that steam-reforming activity may not fully be demonstrated for this amount of support at less than 0.05 % of the weight and it, on the other hand, exceeds 20 % of the weight, the improvement effectiveness of catalytic activity will seldom be accepted considering that amount of support, but it will become disadvantageous economically rather. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this ruthenium is 0.05 – 15 % of the weight, and 0.1 – 2% of the weight of its range is especially desirable.

[0017] When supporting this ruthenium, it can support by request combining other metals. As these other metals, a zirconium, cobalt, magnesium, etc. are mentioned, for example. the case where it supports combining a ruthenium and a zirconium -- the amount of support of a zirconium -- ZrO_2 ***** -- support criteria -- it is -- usually -- it is more preferably selected in 1 – 15% of the weight of the range 0.5 to 15% of the weight 0.5 to 20% of the weight. moreover, the atomic ratio [as opposed to / when supporting combining a ruthenium and cobalt / a ruthenium in the amount of support of cobalt] of cobalt -- usually -- 0.01–30 -- desirable -- 0.1–30 -- it is selected so that it may be more preferably set to 0.1–10. Furthermore, when supporting combining a ruthenium and magnesium, the amount of support of magnesium is 0.5 – 20 % of the weight usually more preferably selected in 1 – 15% of the weight of the range 0.5 to 15% of the weight on support criteria as MgO . On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesias, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable.

[0018] The catalyst which supported the ruthenium to the zirconia is mentioned as one of the desirable modes of the steam-reforming catalyst used by this invention. The zirconia (ZrO_2) of a simple substance is sufficient as this zirconia, and the fully stabilized zirconia containing a stabilization component like a magnesia is sufficient as it. As this fully stabilized zirconia, a thing including a magnesia, yttria, Seria, etc. is suitable. As one more of the desirable modes of the steam-reforming catalyst used by this invention, the catalyst which supported the cobalt and/or magnesium other than a ruthenium, a zirconium or a ruthenium, and a zirconium to alumina support further can be mentioned. Especially as this alumina, alpha-alumina which is excellent in thermal resistance and a mechanical strength is desirable. a ratio with the carbon which originates in a steam and a hydrocarbon oil as a reaction condition in steam-reforming processing -- S/C (mole ratio) -- usually -- 2–5 -- desirable -- 2–4 -- it is more preferably selected in 2–3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0019] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall via the generated radical, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet

temperature, the range 50–800 degrees C is desirable. If catalyzed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure — usually — pressure 3MPa — desirable — the range of ordinary pressure 1MPa — it is — moreover, LHSV — usually — 0.1–100h⁻¹ — it is the range of 0.2–50h⁻¹ preferably. In order that CO obtained by the above-mentioned steam reforming may have an adverse effect on hydrogen generation in the manufacture approach of the above-mentioned hydrogen, it is CO₂ by the reaction about this. It is desirable to carry out and to remove CO. Thus, the hydrogen for fuel cells can be manufactured efficiently.

[0020]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, in the example and the example of a comparison, what is shown below as kerosene and an oxidizer was used.

(1) It has 153 degrees C of kerosene initial boiling points, 176 degrees C of 10% distillation temperatures, 194 degrees C of 30% distillation temperatures, 209 degrees C of 50% distillation temperatures, 224 degrees C of 70% distillation temperatures, 249 degrees C of 90% distillation temperatures, and the distillation curve of 267 degrees C of terminal points, and the JIS-No. 1 kerosene whose sulfur content is the 48 weight ppm was used.

(2) The oxidizing agent which added and prepared 13.6g of salicylic acids in ordinary temperature to 500ml of hydrogen peroxide solution of the 5 % of the weight concentration of oxidizing agents was used. Moreover, the micro channel reactor used in the example has 100 micrometers long, the side of 100 micrometers, and eight die length of 90mm.

[0021] 500ml of example 1JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, when separation recovery of the part for kerosene was carried out and sulfur concentration was analyzed, it was the 0.51 weight ppm.

[0022] 500ml of example 2JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with what calcinated 15ml of nickel support diatomaceous earth catalysts as a devulcanizing agent. After carrying out temperature up of this to 120 degrees C under ordinary pressure and in the hydrogen air current and holding at 120 degrees C for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth catalyst was activated. Then, the temperature was lowered at 150 degrees C and it held to the temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil by liquid-space-velocity 10h⁻¹ under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 0.13 weight ppm.

[0023] 500ml of example 3JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24

hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with 15ml of Ag support silica-alumina catalysts as a devulcanizing agent. Temperature up of this was carried out to 170 degrees C under ordinary pressure and in the nitrogen air current, and after holding at 170 degrees C for 3 hours, the temperature was lowered to the room temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil on condition that a room temperature and liquid-space-velocity 10h^{-1} under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 0.15 weight ppm.

[0024] 2l. of oxidizers was mixed with 2l. of example of comparison 1JIS-No. 1 kerosene, it agitated by rotational frequency 100rpm at the room temperature for 4 hours and 10 minutes using the propeller blade rabble, oxidation treatment of kerosene was performed, and oxidation kerosene was obtained. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 2l. of the above-mentioned oxidation kerosene was held in the container with a capacity of 5l., silica gel 200g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, when separation recovery of the part for kerosene was carried out and sulfur concentration was analyzed, it was the 23.1 weight ppm.

[0025] 2l. of oxidizers was mixed with 2l. of example of comparison 2JIS-No. 1 kerosene, it agitated by rotational frequency 100rpm at the room temperature for 4 hours and 10 minutes using the propeller blade rabble, oxidation treatment of kerosene was performed, and oxidation kerosene was obtained. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 2l. of the above-mentioned oxidation kerosene was held in the container with a capacity of 5l., silica gel 200g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with what calcinated 15ml of nickel support diatomaceous earth catalysts as a devulcanizing agent. After carrying out temperature up of this to 120 degrees C under ordinary pressure and in the hydrogen air current and holding at 120 degrees C for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth catalyst was activated. Then, the temperature was lowered at 150 degrees C and it held to the temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil by liquid-space-velocity 10h^{-1} under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 4.5 weight ppm. An example 1, the example 1 of a comparison, and an example 2 and the example 2 of a comparison are compared, and it turns out that it is more effective to use a micro channel reactor rather than the reactor generally used in oxidation treatment so that clearly.

[0026] Example 4 (steam-reforming processing)

Steam-reforming processing of the desulfurization kerosene obtained in the example 2 was carried out with the refining vessel with which 25ml (amount of ruthenium support 0.4 mass %, support criteria) of ruthenium system reforming catalysts was filled up. Refining processing conditions are a pressure:atmospheric pressure, the steam/carbon 2.5 (mole ratio), LHSV:1.0hr⁻¹, inlet temperature:500 degree C, and outlet temperature:750 degree C. Consequently, the invert ratio in the refining outlet of 250 hours after was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this reaction period was below the 0.2 weight ppm.

[0027]

[Effect of the Invention] According to this invention, by oxidizing an organosulfur compound content hydrocarbon oil using a micro channel reactor, oxidation reaction of this sulfur compound can fully be advanced, and can be desulfurized efficiently. By using the hydrocarbon oil by which desulfurization processing was carried out by this approach, the hydrogen for fuel cells can be manufactured efficiently.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the desulfurization approach of a hydrocarbon oil, and the manufacture approach of the hydrogen for fuel cells. This invention relates to the approach of manufacturing the hydrogen for fuel cells efficiently, in more detail using the approach of fully advancing oxidation reaction of this sulfur compound, and desulfurizing it efficiently, and the hydrocarbon oil by which desulfurization processing was carried out by this approach by oxidizing an organosulfur compound content hydrocarbon oil using a micro channel reactor.

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PRIOR ART

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbon oils, such as naphtha of a petroleum system and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan.

[0003] When using a fuel cell for a noncommercial use or automobiles, the above-mentioned hydrocarbon oil is liquefied at ordinary temperature ordinary pressure, and since the distribution system is fixed, it is advantageous [the thing of a petroleum system / a gas station, a dealer, etc.] as sources of hydrogen the top where storage and handling are easy. However, such a hydrocarbon oil has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this hydrocarbon oil, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon oil. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon oil, it needs performing desulfurization processing to this hydrocarbon oil, and making long duration reduce a sulfur content content below in the rear-spring-supporter 1 weight ppm from the point of a catalyst life.

[0004] Conventionally, the sulfur compound contained in it is oxidized with an oxidizer as the desulfurization approach of a petroleum fraction, and in order to promote the reaction of the approach (JP,4-72387,A) of removing using lifting of the melting point or the boiling point or a sulfur compound, and an oxidizer, the method (JP,11-140462,A) of using an oxidation catalyst etc. is learned. However, when applying these approaches to desulfurization of an organosulfur compound content hydrocarbon oil, it is the actual condition that sufficient oxidation effectiveness is not acquired since the sulfur concentration in this hydrocarbon oil is low, and a sulfur content cannot be reduced to practical level. Moreover, in oxidation reaction of a sulfur compound, although to perform mixing with a petroleum fraction and an oxidizing agent and churning using a homogenizer etc. was tried (JP,11-140462,A), since the reaction rate was slow, there was a problem that oxidation reaction could not fully be advanced, in this case.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, by oxidizing an organosulfur compound content hydrocarbon oil using a micro channel reactor, oxidation reaction of this sulfur compound can fully be advanced, and can be desulfurized efficiently. By using the hydrocarbon oil by which desulfurization processing was carried out by this approach, the hydrogen for fuel cells can be manufactured efficiently.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of manufacturing the hydrogen for fuel cells efficiently, using the approach of fully advancing oxidation reaction of this sulfur compound, and desulfurizing an organosulfur compound content hydrocarbon oil efficiently under such a situation, and the hydrocarbon oil by which desulfurization processing was carried out by this approach.

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MEANS

[Means for Solving the Problem] The result of having repeated research wholeheartedly in order that this invention persons might attain the aforementioned object, By removing an organosulfur compound by technique, such as adsorption, an extract, and distillation, and making a devulcanizing agent contact if needed further, after oxidizing an organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor It found out that the hydrogen for fuel cells could be manufactured efficiently that desulfurization processing can be carried out efficiently and by carrying out refining processing of the hydrocarbon oil by which desulfurization processing was carried out by this approach. This invention is completed based on this knowledge.

[0007] Namely, the process at which this invention oxidizes (A) organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor, The organic sulfur oxidation compound obtained at the (B) above-mentioned (A) process And adsorption, an extract, The desulfurization approach of the hydrocarbon oil characterized by giving the process which contact processing liquid with the adsorbent further obtained at the (C) above-mentioned (B) process is contacted to a devulcanizing agent the process which is made to remove by technique, such as distillation, and removes a sulfur compound, and if needed, and removes a residual sulfur compound is offered. Moreover, this invention also offers the manufacture approach of the hydrogen for fuel cells characterized by making a partial oxidation catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst contact, after desulfurizing an organosulfur compound content hydrocarbon oil by said approach.

[0008]

[Embodiment of the Invention] The process which oxidizes (A) organosulfur compound content hydrocarbon oil with an oxidizer in the desulfurization approach of the hydrocarbon oil of this invention, (B) The organosulfur compound in the oxidation-treatment liquid obtained at the above-mentioned (A) process The process which contacts contact processing liquid with the adsorbent further obtained at the (C) above-mentioned (B) process to a devulcanizing agent is given the process which makes (namely, an organic sulfur oxidation compound) remove by technique, such as adsorption, an extract, and distillation, and if needed. As an organosulfur compound content hydrocarbon oil with which the approach of this invention is applied, LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL (Gas to Liquid), a waste plastic oil, biotechnology fuel, etc. can be mentioned, for example.

[0009] In these, kerosene is suitable as a raw material for the hydrogen manufacture for fuel cells. Next, each process is explained.

(A) This process is a process which oxidizes the aforementioned organosulfur compound content hydrocarbon oil with an oxidizer using a micro channel reactor as **. Although the micro channel reactor used in the process concerned is a reactor with the passage of an equivalent diameter smaller than 500 micrometers as indicated by "Erdoel Erdgas Kohle", the 114th volume, and the 578th page (1998), in this invention, 1mm or less of the equivalent diameter of the passage of this reactor is sufficient. Moreover, the micro channel reactor which gave the mixed function can also be used.

[0010] Moreover, as an oxidizing agent, the thiophenes contained in the hydrocarbon oil that what is necessary is just what can oxidize to a sulfoxide or a sulfone. It is not restricted especially. For example, oxygen, air, a nitrogen tetroxide, ozone, chlorine, a bromine, Sodium metaperiodate, a potassium dichromate, potassium permanganate, A chromic anhydride, a hypochlorous acid, a hydrogen peroxide, a peracetic acid, a hydrogen-peroxide + acetic acid, A performic acid, a hydrogen-peroxide + formic acid, a meta-chloro perbenzoic acid, a hydrogen-peroxide + meta-chloro benzoic acid, A fault chloroacetic acid, a hydrogen-peroxide-solution + chloroacetic acid, fault dichloroacetic acid, hydrogen-peroxide + dichloroacetic acid, A fault trichloroacetic acid, a hydrogen-peroxide + trichloroacetic acid, fault trifluoroacetic acid, hydrogen-peroxide + trifluoroacetic acid, fault meta-sulfonic acid, hydrogen-peroxide + meta-sulfonic acid, a fault salicylic acid, a hydrogen-peroxide + salicylic acid, persulfuric acid, a hydrogen-peroxide + sulfuric acid, etc. can be used. One sort of these oxidizers may be used and they may be used combining two or more sorts. Moreover, the amount of the oxidizer used should just be at least 1Eq to 1Eq of organosulfur compounds in a hydrocarbon oil. Although a room temperature is enough as oxidation-treatment temperature, it may warm suitably as occasion demands and you may oxidize.

[0011] (B) Contact the oxidation-treatment liquid obtained at the process aforementioned (A) process to an adsorbent, and explain the process which carries out adsorption treatment of the sulfur compound. As an adsorbent used in the process concerned, a porosity inorganic oxide, activated carbon, porosity insolubility synthetic resin, etc. are mentioned. These adsorbents may come to support a suitable metallic element. As the above-mentioned porosity inorganic oxide, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, clay, clay, diatomaceous earth, etc. are mentioned preferably, for example. Although there is especially no limit as a configuration of this adsorbent, the configuration of powder, a pellet, a tablet, a bead, etc. is desirable.

[0012] In this invention, one sort of said adsorbent may be used and it may be used combining two or more sorts. As temperature at the time of contacting a hydrocarbon oil to this adsorbent, the range of -40-100 degrees C is desirable. If there is a possibility that the fluidity of a hydrocarbon oil may fall at less than -40 degrees C, and this temperature may become inadequate [the adsorption treatment of a sulfur compound] and it exceeds 100 degrees C, there is an inclination for the adsorption capacity of an adsorbent to fall and it is not desirable.

[0013] (C) It is the process which ** is the process to which this process is given if needed, contacts contact processing liquid with the adsorbent obtained at the aforementioned (B) process to a devulcanizing agent, and removes a residual sulfur compound. By giving this process, the sulfur content content in a hydrocarbon oil can be reduced further. There is especially no limit as a devulcanizing agent used for the process concerned, and an adsorption devulcanizing agent other than an adsorbent, a hydrodesulfurization catalyst, etc. in the aforementioned (B) process can be used. The catalyst which comes at least to support a kind of metallic element chosen, for example from nickel, Ag, Cr, Mn, Fe, Co, Cu, Zn, Pd, Ir, Pt, Ru, Rh, and Au to porosity support here as an adsorption devulcanizing agent other than the adsorbent in the aforementioned (B) process is desirable. The catalyst which comes to support especially nickel and/or Ag is suitable. These adsorption devulcanizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction processing beforehand. Moreover, when using a hydrodesulfurization catalyst as this devulcanizing agent, little addition of the hydrogen can be carried out.

[0014] In this invention, one sort of said devulcanizing agent may be used and it may be used combining two or more sorts. As temperature at the time of contacting a hydrocarbon oil to this devulcanizing agent, the range of -40-220 degrees C is desirable. If there is a possibility that the fluidity of a hydrocarbon oil may fall at less than -40 degrees C, and it may become inadequate desulfurization removing [of a sulfur compound] this temperature and it exceeds 220 degrees C, there is an inclination for the adsorption capacity of a devulcanizing agent to fall, and it is not desirable. Thus, the sulfur content in an organosulfur compound content hydrocarbon oil can be more preferably reduced below in the 0.2 weight ppm below the 0.5 weight ppm below the 1 weight ppm.

[0015] In the manufacture approach of the hydrogen for fuel cells is invention, after desulfurizing an organosulfur compound content hydrocarbon oil by the above-mentioned approach, the hydrogen for fuel cells is manufactured by making an autothermal reforming catalyst, a partial oxidation catalyst, or a steam-reforming catalyst contact. As these autothermal reforming catalysts, a partial oxidation catalyst, or a steam-reforming catalyst, a nickel system or a ruthenium system catalyst is suitable. Moreover, although a well-known approach can be conventionally used as a partial oxidation method, autothermal reforming, and a steam reforming process, a steam reforming process is advantageous in these.

[0016] Next, the manufacture approach of the hydrogen by the steam reforming process is explained. As a steam-reforming catalyst used in this steam reforming process, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. The above-mentioned support metal may make a kind support, and may be made to support combining two or more sorts. In these catalysts, the thing (ruthenium system catalyst) which made especially the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large. In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 - 20% of the weight of the desirable range on support criteria. If there is a possibility that steam-reforming activity may not fully be demonstrated for this amount of support at less than 0.05 % of the weight and it, on the other hand, exceeds 20 % of the weight, the improvement effectiveness of catalytic activity will seldom be accepted considering that amount of support, but it will become disadvantageous economically rather. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this ruthenium is 0.05 - 15 % of the weight, and 0.1 - 2% of the weight of its range is especially desirable.

[0017] When supporting this ruthenium, it can support by request combining other metals. As these other metals, a zirconium, cobalt, magnesium, etc. are mentioned, for example. the case where it supports combining a ruthenium and a zirconium -- the amount of support of a zirconium -- ZrO_2 ***** -- support criteria -- it is -- usually -- it is more preferably selected in 1 - 15% of the weight of the range 0.5 to 15% of the weight 0.5 to 20% of the weight. moreover, the atomic ratio [as opposed to / when supporting combining a ruthenium and cobalt / a ruthenium in the amount of support of cobalt] of cobalt -- usually -- 0.01-30 -- desirable -- 0.1-30 -- it is selected so that it may be more preferably set to 0.1-10. Furthermore, when supporting combining a ruthenium and magnesium, the amount of support of magnesium is 0.5 - 20 % of the weight usually more preferably selected in 1 - 15% of the weight of the range 0.5 to 15% of the weight on support criteria as MgO . On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesias, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable.

[0018] The catalyst which supported the ruthenium to the zirconia is mentioned as one of the desirable modes of the steam-reforming catalyst used by this invention. The zirconia (ZrO_2) of a simple substance is sufficient as this zirconia, and the fully stabilized zirconia containing a stabilization component like a magnesia is sufficient as it. As this fully stabilized zirconia, a thing including a magnesia, yttria, Seria, etc. is suitable. As one more of the desirable modes of the steam-reforming catalyst used by this invention, the catalyst which supported the cobalt and/or magnesium other than a ruthenium, a zirconium or a ruthenium, and a zirconium to alumina support further can be mentioned. Especially as this alumina, alpha-alumina which is excellent in thermal resistance and a mechanical strength is desirable. a ratio with the carbon which originates in a steam and a hydrocarbon oil as a reaction condition in steam-reforming processing -- S/C (mole ratio) -- usually -- 2-5 -- desirable -- 2-4 -- it is more preferably selected in 2-3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0019] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall via the generated radical, and operation

may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650–800 degrees C is desirable. If catalyst bed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure — usually — pressure — 3MPa — desirable —
- the range of ordinary pressure — 1MPa — it is — moreover, LHSV — usually — 0.1–100h⁻¹ —
- it is the range of 0.2–50h⁻¹ preferably. In order that CO obtained by the above-mentioned steam reforming may have an adverse effect on hydrogen generation in the manufacture approach of the above-mentioned hydrogen, it is CO₂ by the reaction about this. It is desirable to carry out and to remove CO. Thus, the hydrogen for fuel cells can be manufactured efficiently.

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EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, in the example and the example of a comparison, what is shown below as kerosene and an oxidizer was used.

(1) It has 153 degrees C of kerosene initial boiling points, 176 degrees C of 10% distillation temperatures, 194 degrees C of 30% distillation temperatures, 209 degrees C of 50% distillation temperatures, 224 degrees C of 70% distillation temperatures, 249 degrees C of 90% distillation temperatures, and the distillation curve of 267 degrees C of terminal points, and the JIS-No. 1 kerosene whose sulfur content is the 48 weight ppm was used.

(2) The oxidizing agent which added and prepared 13.6g of salicylic acids in ordinary temperature to 500ml of hydrogen peroxide solution of the 5 % of the weight concentration of oxidizing agents was used. Moreover, the micro channel reactor used in the example has 100 micrometers long, the side of 100 micrometers, and eight die length of 90mm.

[0021] 500ml of example 1 JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, when separation recovery of the part for kerosene was carried out and sulfur concentration was analyzed, it was the 0.51 weight ppm.

[0022] 500ml of example 2 JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with what calcinated 15ml of nickel support diatomaceous earth catalysts as a devulcanizing agent. After carrying out temperature up of this to 120 degrees C under ordinary pressure and in the hydrogen air current and holding at 120 degrees C for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth catalyst was activated. Then, the temperature was lowered at 150 degrees C and it held to the temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil by liquid-space-velocity 10h-1 under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 0.13 weight ppm.

[0023] 500ml of example 3 JIS-No. 1 kerosene and 500ml of oxidizing agents were independently introduced in each channel of a micro channel reactor the rate for 0.25ml/by the syringe pump, respectively, oxidation treatment of kerosene was performed at the room temperature, and

oxidation kerosene was obtained. The processing times of the kerosene in this case were 4 hours and 10 minutes. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 500ml of the above-mentioned oxidation kerosene was held in the container with a capacity of 2l., silica gel 50g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with 15ml of Ag support silica-alumina catalysts as a devulcanizing agent. Temperature up of this was carried out to 170 degrees C under ordinary pressure and in the nitrogen air current, and after holding at 170 degrees C for 3 hours, the temperature was lowered to the room temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil on condition that a room temperature and liquid-space-velocity 10h⁻¹ under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 0.15 weight ppm.

[0024] 2l. of oxidizers was mixed with 2l. of example of comparison 1JIS-No. 1 kerosene, it agitated by rotational frequency 100rpm at the room temperature for 4 hours and 10 minutes using the propeller blade rabble, oxidation treatment of kerosene was performed, and oxidation kerosene was obtained. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 2l. of the above-mentioned oxidation kerosene was held in the container with a capacity of 5l., silica gel 200g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, when separation recovery of the part for kerosene was carried out and sulfur concentration was analyzed, it was the 23.1 weight ppm.

[0025] 2l. of oxidizers was mixed with 2l. of example of comparison 2JIS-No. 1 kerosene, it agitated by rotational frequency 100rpm at the room temperature for 4 hours and 10 minutes using the propeller blade rabble, oxidation treatment of kerosene was performed, and oxidation kerosene was obtained. Next, after separating the oxidation kerosene and the oxidizer which were obtained, the 2l. of the above-mentioned oxidation kerosene was held in the container with a capacity of 5l., silica gel 200g was added to this, and it agitated at the room temperature for 24 hours. Subsequently, separation recovery of the part for kerosene was carried out. On the other hand, the coil made from stainless steel with a bore of 17mm was filled up with what calcinated 15ml of nickel support diatomaceous earth catalysts as a devulcanizing agent. After carrying out temperature up of this to 120 degrees C under ordinary pressure and in the hydrogen air current and holding at 120 degrees C for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth catalyst was activated. Then, the temperature was lowered at 150 degrees C and it held to the temperature. Next, the aforementioned kerosene which carried out separation recovery was circulated to the coil by liquid-space-velocity 10h⁻¹ under ordinary pressure. When the sulfur concentration in the kerosene after 5-hour progress was analyzed, it was the 4.5 weight ppm. An example 1, the example 1 of a comparison, and an example 2 and the example 2 of a comparison are compared, and it turns out that it is more effective to use a micro channel reactor rather than the reactor generally used in oxidation treatment so that clearly.

[0026] Example 4 (steam-reforming processing)

Steam-reforming processing of the desulfurization kerosene obtained in the example 2 was carried out with the refining vessel with which 25ml (amount of ruthenium support 0.4 mass %, support criteria) of ruthenium system reforming catalysts was filled up. Refining processing conditions are a pressure:atmospheric pressure, the steam/carbon 2.5 (mole ratio), LHSV:1.0hr⁻¹, inlet temperature:500 degree C, and outlet temperature:750 degree C. Consequently, the invert ratio in the refining outlet of 250 hours after was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this reaction period was below the 0.2 weight ppm.

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